Novel *ipso*-Substitution of *p*-Sulfinylphenols through the Pummerer-Type Reaction: A Selective and Efficient Synthesis of *p*-Quinones and Protected *p*-Dihydroquinones

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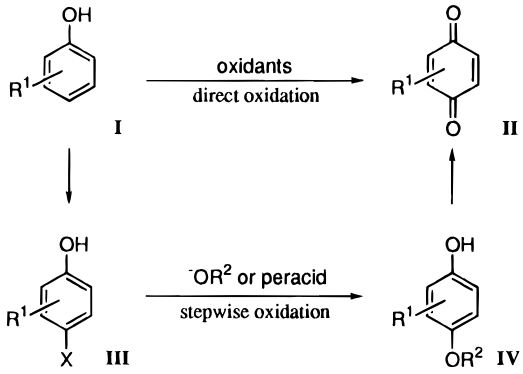
The treatment of *p*-sulfinylphenols **3a**−**q** with trifluoroacetic anhydride caused a Pummerer-type reaction on aromatic rings and concomitant desulfurization to give mixtures of the corresponding *p*-dihydroquinones **9** and *p*-quinones **10**, which were subsequently oxidized under mild conditions to provide high yields of *p*-quinones **10**. On the other hand, the treatment of *p*-(phenylsulfinyl)-phenyl ethers **6** with trifluoroacetic anhydride in the presence of styrene caused the direct *ipso*-substitution of the sulfinyl groups into trifluoroacetoxy groups, giving the protected dihydroquinones **14** in high yields. Both types of reactions were generally completed below room temperature within 1 h and compatible with various functional groups such as the allyl, carbonyl, ester, amide, and silyloxy groups. The preparation of the *p*-sulfinylphenols **3** and the silyl ethers **6** is also described through *p*-specific thiocyanation of phenols followed by the Grignard reaction and oxidation.

Introduction

The transformation of phenols and their derivatives **I** into *p*-quinones **II** or *p*-dihydroquinone derivatives **IV** is very important for the synthesis of *peri*-hydroxy polyaromatic quinone compounds having remarkable biological activities.[1] For this purpose, direct oxidation of **I** using various oxidants and the functionalization of the *para*-position of **I** followed by functional group transformation (**III** → **IV**) have been developed (Scheme 1). Direct oxidation is usually performed using Fremy's salt,[2] ceric ammonium nitrate,[1a,c,3] lead tetraacetate,[4] thallium(III) nitrate,[5] hypervalent iodine(III) compounds,[1a,6] etc.[7] However, it sometimes suffers from low reproducibility,[4c] *ortho*-oxidation,[2c] or other side reactions.[7k] Furthermore, it is inefficient for the oxidation of some phenols having electron-withdrawing groups.[7d] On the other hand, stepwise oxidation is usually carried out *via* the intermediates **III** (X = N_2^+,[8] COR,[9] halogen,[10−12] $SiMe_2SiMe_3$[13]) and features a promising preparation of the protected *p*-dihydroquinone derivatives **IV**, useful intermediates for total syntheses of polycyclic quinones. The *ipso*-substitution reactions, however, need fairly strong reaction conditions including high temperature,[11,12] strong basic conditions,[10] or oxidation conditions,[9,13] and many of them are inconsistent with the presence of other reactive functional groups such as carbonyl groups.[11,12b,c] Therefore, an alternative mild and efficient synthesis of the quinones is required.

Scheme 1



Our concept to develop a novel synthesis of the quinones is based on the following. The treatment of

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(1) For recent examples, see: (a) Bergeron, D.; Brassard, P. *Heterocycles* **1992**, *34*, 1835. (b) Brimble, M. A.; Phythian, S. J. *Tetrahedron Lett.* **1993**, *34*, 5813. (c) Magnus, P.; Eisenbeis, S. A. Magnus, N. A. *J. Chem. Soc., Chem. Commun.* **1994**, 1545. (d) Nicolaou, K. C.; Gross, J. L.; Kerr, M. A.; Lemus, R. H.; Ikeda, K.; Ohe, K. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 781.

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(4) (a) Bubb, W. A.; Sternhell, S. *Tetrahedron Lett.* **1970**, 4499. (b) Tamura, Y.; Sasho, M.; Akai, S.; Wada, A.; Kita, Y. *Tetrahedron* **1984**, *40*, 4539. (c) Tamura, Y.; Sasho, M.; Akai, S.; Kishimoto, H.; Sekihachi, J.; Kita, Y. *Tetrahedron Lett.* **1986**, *27*, 195.

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(6) (a) Barret, R.; Daudon, M. *Tetrahedron Lett.* **1990**, *31*, 4871. (b) Barret, R.; Daudon, M. *Synth. Commun.* **1990**, *20*, 2907.

(7) $K_2S_2O_8$: (a) Gleim, R. D.; Trenbeath, S.; Suzuki, F.; Sih, C. J. *J. Chem. Soc., Chem. Commun.* **1978**, 242. (b) Jain, A. C.; Singh, P. K.; Bhojak, N. *Indian J. Chem.* **1994**, *B33*, 372. NH_4NO_3-TFAA: (c) Boeckman, R. K.; Cheon, S. H. *J. Am. Chem. Soc.* **1983**, *105*, 4112. (d) Croisy-Delcey, M.; Bisagni, E.; Huel, C.; Zilberfarb, D.; Croisy, A. *J. Heterocycl. Chem.* **1991**, *28*, 65. Salcomine−O_2: (e) Wakamatsu, T.; Nishi, T.; Ohnuma, T.; Ban, Y. *Synth. Commun.* **1984**, *14*, 1167. (f) Bloomer, J. L.; Stagliano, K. W. *Tetrahedron Lett.* **1993**, *34*, 757. NBS−AcOH: (g) Boyd, V. A.; Sulikowski, G. A. *J. Am. Chem. Soc.* **1995**, *117*, 8472. AgO−HNO_3: (h) Kraus, G. A.; Chen, L. *Synlett* **1991**, 51. (i) Brimble, M. A.; Phythian, S. J. *Tetrahedron Lett.* **1993**, *34*, 5813. H_2O_2−hetero polyacid: (j) Shimizu, M.; Orita, H.; Hayakawa, T.; Takehira, K. *Tetrahedron Lett.* **1989**, *30*, 471. See also: (k) Majetich, G.; Zhang, Y. *J. Am. Chem. Soc.* **1994**, *116*, 4979.

(8) For an example, see: Yoneda, N.; Fukuhara, T.; Mizokami, T.; Suzuki, A. *Chem. Lett.* **1991**, 459.

(9) (a) Syper, L. *Synthesis* **1989**, 167. (b) Matsumoto, M; Kobayashi, H.; Hotta, Y. *J. Org. Chem.* **1984**, *49*, 4740.

(10) For an example, see: Watanabe, M.; Shinoda, E.; Shimizu, Y.; Furukawa, S.; Iwao, M.; Kuraishi, T. *Tetrahedron* **1987**, *43*, 5281.

(11) Bacon, R. G. R.; Rennison, S. C. *J. Chem. Soc. C* **1969**, 312.

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(13) Suginome, M.; Matsunaga, S.; Ito, Y. *Synlett* **1995**, 941.

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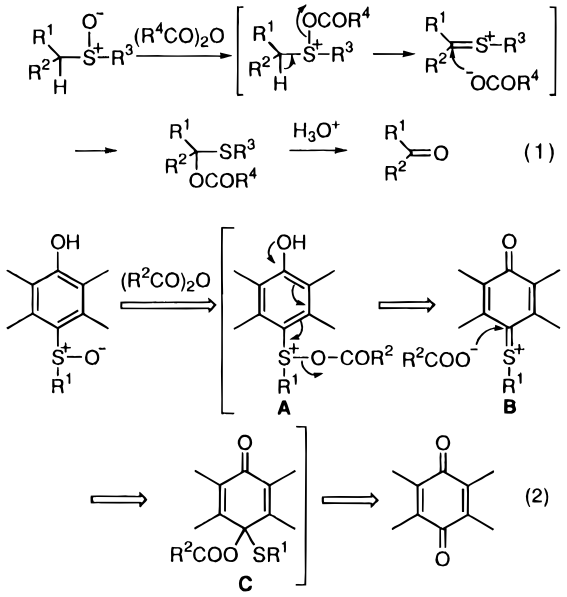
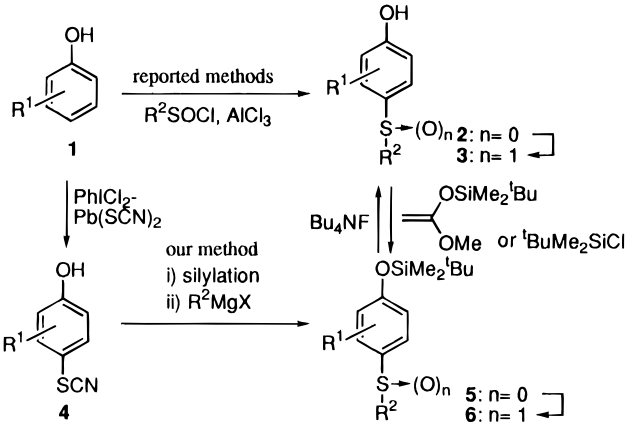
Scheme 2



aliphatic sulfoxides with acid anhydrides causes the Pummerer rearrangement to give α-acyloxy sulfides. Since these products can be easily hydrolyzed to carbonyl compounds, the overall reaction provides a convenient method for the transformation of sulfinyl groups into carbonyl groups (eq 1 in Scheme 2).[14,15] If similar sequential reactions occur in *p*-sulfinylphenols, this could provide the α-acyloxy sulfide **C** through intermediates **A** and **B**, in which the electron-donating hydroxy group at the *para*-position would strongly accelerate the S−O bond fission in **A** and an appropriate hydrolysis of **C** would give the desired *p*-quinone (eq 2). However, the possibility of such a reaction has not been studied in detail. A related study was reported by King on the reaction of 3,5-dimethyl-4-(methylsulfinyl)phenol with acid anhydrides giving the 2-(acyloxy)-4-sulfenylphenol.[16] Recently, Jung reported inter- and intramolecular nucleophilic addition to the sulfonium ions generated from 4-methyl-2-(arylsulfinyl)phenols.[17,18] In these reactions, the main products were obtained through conjugate addition of nucleophiles at the *meta*-position of the sulfinyl group of the sulfonium ions. Moreover, although there are some synthetic methods for the preparation of the starting *p*-sulfinylphenols,[19] they often have some restrictions. Recently, we published preliminary communications showing the novel and selective preparation of *p*-quinones **II**[20] and suitably protected *p*-dihydroquinones **IV**[21] from *p*-sulfinylphenols **III** (X = SOPh) and their ethers, respectively. These reactions were achieved through an unprecedented *ipso*-substitution of the sulfinyl group into oxygen functional groups below room temperature within 1 h and feature the compatibility with various functional groups including carbonyl groups. In this paper, we report the full account of these studies along with the *p*-specific introduction of the sulfinyl group into the phenols **I**.

Scheme 3. General Preparation of the *p*-Sulfinylphenols 3 and the Ethers 6



Results and Discussions

Preparation of the Starting *p*-Sulfinylphenols. Introduction of the sulfinyl group into the *para*-position of phenols by direct sulfinylation was reported by the use of the sulfinyl chlorides and $AlCl_3$.[19a] However, this method was useful only for limited substrates. For example, 2,3,5,6-tetramethyl-4-(phenylsulfinyl)phenol (**3a**) was prepared from 2,3,5,6-tetramethylphenol by the treatment with PhSOCl and $AlCl_3$ in CH_2Cl_2 at 0 °C in 70% yield, but this method is not preferable for the *o*-unsubstituted phenols like **3i** due to competitive reaction at the *ortho*-position.[19a] By using this method, phenols having $AlCl_3$-sensitive functional groups and electron-withdrawing groups suffered from incompatibility of such functional groups and low reactivity, respectively. Other known methods[19b−d] were not appropriate to the preparation of the functionalized *p*-sulfinylphenols described here. Therefore, we have elucidated the novel and promising *p*-sulfinylation of phenols based on successive thiocyanation, reaction with Grignard reagent, and oxidation (Scheme 3).

The first step, the *p*-specific thiocyanation of phenols **1**, was done in 58−94% yields according to our previous report[22] using $PhICl_2$ and $Pb(SCN)_2$ in CH_2Cl_2 at 0 °C. The second step, the reaction of **4** with the Grignard reagent, required extensive investigation because the yields of the corresponding *p*-sulfenylphenols **2** were unsatisfactory in almost all cases. For example, the treatment of *p*-thiocyanatophenol (**4i**) with PhMgBr gave the *p*-sulfenylphenol **2i** in 50% yield, along with 42% yield of the byproduct **8i** (Scheme 4). On the other hand, a similar Grignard reaction of the *O*-silylated compound

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(16) King, R. R. *J. Org. Chem.* **1978**, *43*, 3784.

(17) Jung, M. E.; Kim, C.; Bussche, L. v. d.; Bussche, L. *J. Org. Chem.* **1994**, *59*, 3248.

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(19) Although direct introduction of the *p*-sulfinyl groups into the phenols was reported, it is limited to simple phenols having alkyl substituents. (a) Chasar, D. W.; Pratt, T. M. *Phosphorus Sulfur* **1978**, *5*, 35. (b) Hilbert, G. E.; Johnson, T. B. *J. Am. Chem. Soc.* **1929**, *51*, 1526. (c) Ranken, P. F.; McKinnie B. G. *Synthesis* **1984**, 117. (d) Wehry, E. J. *J. Am. Chem. Soc.* **1967**, *89*, 41.

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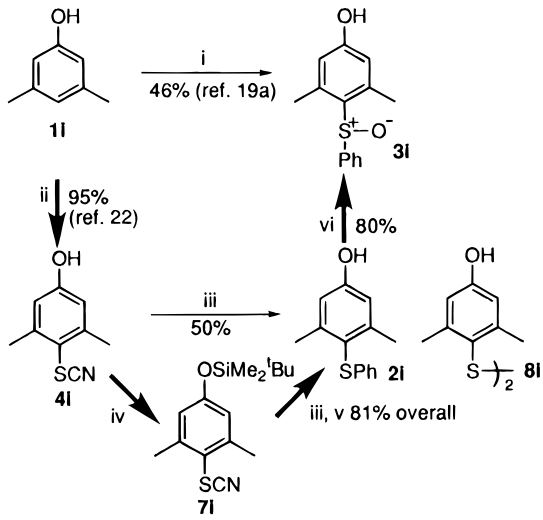
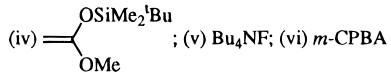
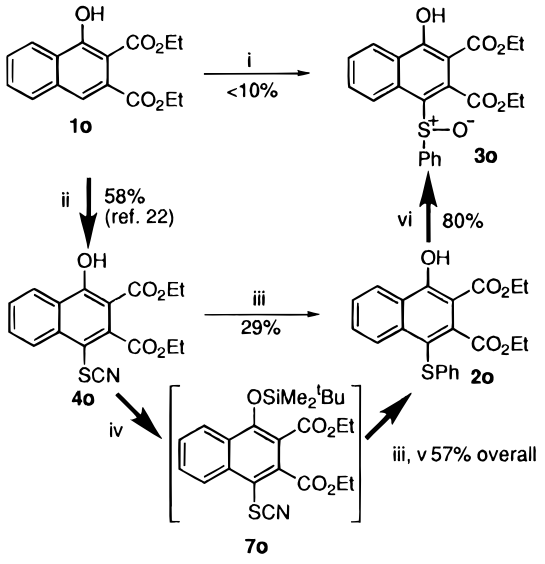
Scheme 4. Preparation of 3i[a]



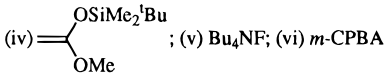
[a]Reagents (i) $PhSOCl$, $AlCl_3$; (ii) $PhICl_2$, $Pb(SCN)_2$; (iii) PhMgBr



Scheme 5. Preparation of 3o[a]



[a]Reagents (i) $PhSOCl$, $AlCl_3$; (ii) $PhICl_2$, $Pb(SCN)_2$; (iii) PhMgBr



7i almost quantitatively gave the *p*-sulfenylphenol ethers,[23,24] which was easily desilylated to give **2i** in 81% yield from **4i**. Another example is shown for the preparation of **3o** having ester groups (Scheme 5). Because of the instability of the silyl ether **7o**, the one-pot silylation of **4o** using *O*-silyl ketene acetal[25] followed by Grignard reaction and desilylation enabled us to get a good yield of **3o**. Neither the direct sulfinylation of **1o** nor the Grignard reaction of the phenol **4o** was satisfactory.

Generally, interconversion between **3** and **6** is achieved in high yields, and the oxidation of the sulfides **2** and **5** into the sulfoxides **3** and **6**, respectively, was achieved using *m*-CPBA at −30 °C in ≥80% yields. Thus, the *p*-sulfinylphenols **3** and the ethers **6** were prepared *via* the thiocyanates **4** in modest to good yields as summarized in Scheme 3.[26,27]

Synthesis of *p*-Quinones. We first investigated the reaction of 2,3,5,6-tetramethyl-4-(phenylsulfinyl)phenol (**3a**) with several acid anhydrides. Although the reaction of **3a** with 10 equiv of acetic anhydride in refluxing 1,2-dichloroethane did not proceed at all (run 1 in Table 1), the reaction of **3a** with 10 equiv of trifluoroacetic anhydride (TFAA) in CH_2Cl_2 occurred immediately at 0 °C. A 1:1 mixture of the dihydroquinone mono(trifluoroacetate) **9a** (A = $COCF_3$) and the benzoquinone **10a** was directly and almost quantitatively obtained. Concentration of the reaction mixture followed by treatment with saturated $NaHCO_3$ in MeOH for 1 h caused hydrolysis of **9a** and subsequent auto-oxidation to give **10a** in 84% yield (method A, run 2, Table 1). The addition of MnO_2,[28] a mild oxidizing reagent of dihydroquinones into *p*-quinones, to the above reaction mixture directly gave **10a** in 62% yield (method B). A similar reaction of **3a** with trifluoromethanesulfonic anhydride (10 equiv) with or without sodium acetate (10 equiv) also provided **10a** in lower yield (60−64%) along with formation of the sulfide **2** (R = H, OAc) in 29−31% yields (runs 3 and 4, Table 1). Using this method, in runs 2−4 (Table 1), 58−96% yields of diphenyl disulfide were formed as a byproduct, which were comparable to the yields of **10a**. Thus, reactive acid anhydrides, particularly trifluoroacetic anhydride, were found to very quickly cause the Pummerer-type reaction of the *p*-sulfinylphenol **3a** and the concomitant desulfurization leading to the oxygen-substituted products **9a** and **10a**.

As summarized in Table 2, various (arylsulfinyl)- **3b**−**e** and (alkylsulfinyl)phenols **3f,g** were readily converted into the *p*-quinone **10a** in high yields by methods A and B (runs 2−7, Table 2); however, the *p*-nitrophenyl derivative **3h** provided only a 10% yield of **10a** (run 8, Table 2). Among these results, the *p*-(phenylsulfinyl)phenol **3a** was found to be the most suitable substrate for this Pummerer-type reaction in terms of its yield and ready availability.

In a like manner, the sulfoxide **3m** having a primary hydroxy group and the sulfoxides **3n**−**q** having ester and amide groups were converted into the quinones **10f**−**j** in 61−90% yields (runs 13−17, Table 2). However, a similar treatment of the *o*-unsubstituted *p*-sulfinylphenol **3i** or the *o*-allylphenol **3l** under the standard conditions did not give the desired *p*-quinones but produced the bis-(trifluoroacetoxy)phenyl sulfide **11** and the *p*-dihydroquinone **12** having a 3-(phenylthio)-2-(trifluoroacetoxy)-

(23) Reactions of alkyl and aryl thiocyanates with Grignard reagents have been thought to be useless due to the competitive reaction at the sulfur and the carbon atoms of the thiocyanato groups.[24a] Zamojski *et al.*, however, recently showed that the reaction of sugar thiocyanates with alkyl- and arylmagnesium reagents occurred at the sulfur atom to give the thioethers in good yields.[24b] We also elucidated that protection of the hydroxy group of the phenol is essential to control the reaction only at the sulfur atom of the thiocyanate. Very recently, Still *et al.* reported that aryl *tert*-butyl sulfides were obtained by the reaction of aryl thiocyanates with $(t\text{-Bu})_2Cu(CN)Li_2$.[24c]

(24) (a) Adams, R.; Bramlet, H. B.; Tendick, F. H. *J. Am. Chem. Soc.* **1920**, *42*, 2369. (b) Pakulski, Z.; Pierozynski, D.; Zamojski, A. *Tetrahedron* **1994**, *50*, 2975. (c) Toste, F. D.; Still, I. W. J. *Tetrahedron Lett.* **1995**, *36*, 4361.

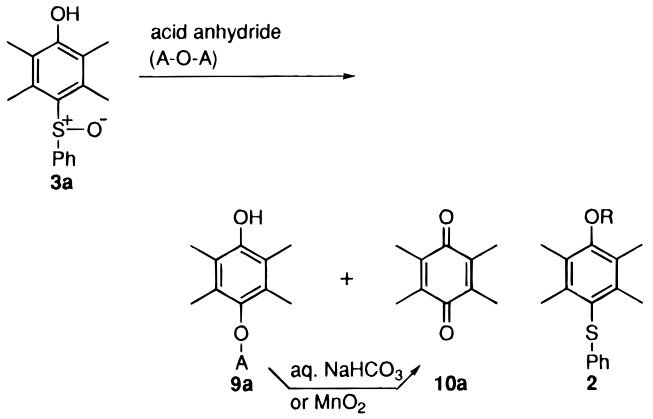
(25) Kita, Y.; Haruta, J.; Segawa, J.; Tamura, Y. *Tetrahedron Lett.* **1979**, 4311.

(26) Recent papers also presented the effective preparation of fused phenol derivatives having *p*-sulfenyl groups by the anionic cycloaddition of thiophthalides[27a] or *o*-[bis(ethylthio)methyl]benzoate[27b] to α,β-unsaturated carbonyl compounds.

(27) (a) Majumdar, G.; Pal, R.; Murty, K. V. S. N.; Mal. D. *J. Chem. Soc., Perkin Trans. 1* **1994**, 309. (b) Ozaki, Y.; Imaizumi, K.; Okamura, K.; Morozumi, M.; Hosoya, A.; Kim, S.-W. *Chem. Pharm. Bull.* **1996**, *44*, 1785.

(28) Cassis, R.; Valderrama, J. A. *Synth. Commun.* **1983**, *13*, 347.

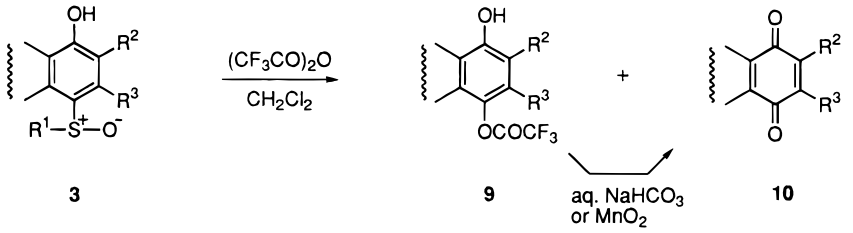
Table 1. Conversion of the *p*-Sulfinylphenol 3a into the Quinone 10a Using Various Acid Anhydrides

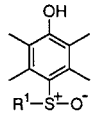
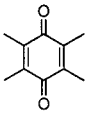
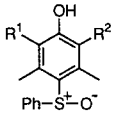
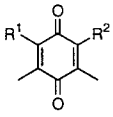
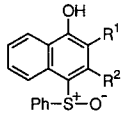
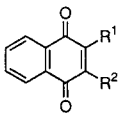


run	reaction condns	yield (%) of **10a** method A[a]	yield (%) of **10a** method B[b]	**2**
1	Ac_2O, $ClCH_2CH_2Cl$, reflux, 2 h	N.D.[c]		N.D.
2	$(CF_3CO)_2O$, CH_2Cl_2, 0 °C, 5 min	84[d]	62	N.D.
3	$(CF_3SO_2)_2O$, CH_2Cl_2, 0 °C, 5 min	64[d]		29 (R = H)[a]
4	$(CF_3SO_2)_2O$, AcONa, MeCN, 0 °C, 5 min	60[d]		31 (R = Ac)[a]

[a] Worked up with aqueous $NaHCO_3$ in MeOH. [b] MnO_2 was added to the reaction mixture. [c] **3a** was almost quantitatively recovered. [d] Diphenyl disulfide was isolated in 96 (run 2), 58 (run 3) and 60% yields (run 4), respectively. N.D. = not detected.

Table 2. Conversion of Various *p*-Sulfinylphenols 3 to the Corresponding Quinones 10



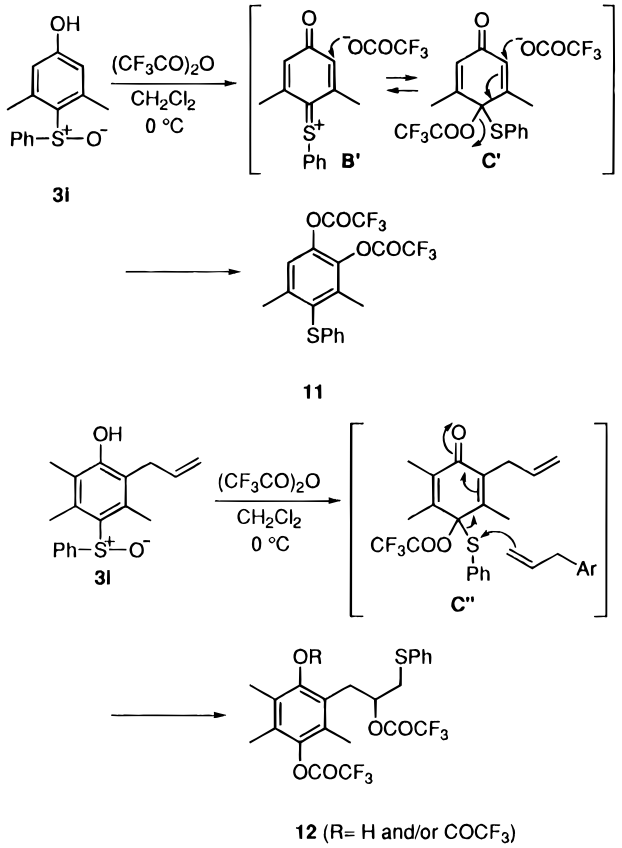
Run	Substrate **3**		Reaction conditions	Product **10**		Yield (%) Method A[a]	Yield (%) Method B[b]
1		**a** R^1 = Ph	0 °C, 5 min		**a**	84	62
2		**b** R^1 = C_6H_4-*p*-OMe	//		//	73	65
3		**c** R^1 = C_6H_4-*p*-Me	//		//	68	
4		**d** R^1 = C_6H_4-*p*-Cl	//		//	74	
5		**e** R^1 = C_6H_4-*p*-F	//		//	70	66
6		**f** R^1 = Me	0 °C,15 min		//	76	76
7		**g** R^1 = ^{t}Bu	0 °C, 5 min		//	61	
8		**h** R^1 = C_6H_4-*p*-NO_2	//		//	10	
9		**i** R^1 = R^2 = H	0 °C, 5 min[c]		**b** R^1 = R^2 = H	63	
10		**j** R^1 = Me, R^2 = H	// [c]		**c** R^1 = Me, R^2 = H	84	
11		**k** R^1 = Me, R^2 = COMe	// [c]		**d** R^1 = Me, R^2 = COMe	80	
12		**l** R^1 = Me, R^2 = $CH_2CH{=}CH_2$	// [c]		**e** R^1 = Me, R^2 = $CH_2CH{=}CH_2$	75	
13		**m** R^1 = Me, R^2 = $(CH_2)_3OH$	//		**f** R^1 = Me, R^2 = $(CH_2)_3OH$	75	
14		**n** R^1 = CO_2Et, R^2 = Me	-30 °C, 10 min		**g** R^1 = CO_2Et, R^2 = Me		90
15		**o** R^1 = R^2 = CO_2Et	//		**h** R^1 = R^2 = CO_2Et		86
16		**p** R^1 = $CONEt_2$, R^2 = Me	0 °C, 10 min		**i** R^1 = $CONEt_2$, R^2 = Me		81
17		**q** R^1 = R^2 = $CONEt_2$	-30 °C → r.t., 1 h		**j** R^1 = R^2 = $CONEt_2$		61

[a] Worked up with aqueous $NaHCO_3$ in MeOH. [b] MnO_2 was added. [c] Allyltrimethylsilane (10 equiv) was added.

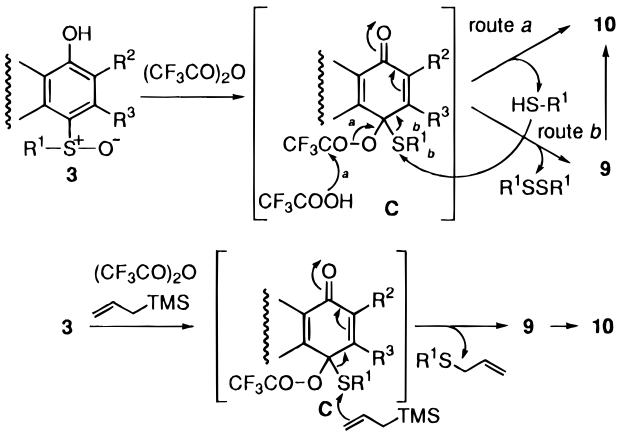
propyl side chain in 57% and about 50% yields, respectively (Scheme 6). Compound **11** may be formed through the intermediates **B′** and **C′** as previously reported in a similar reaction.[16] The formation of **12** implied the attack of another molecule at the sulfur atom of intermediate **C″**. The addition of an external nucleophile that effectively attacks the sulfur atom of intermediate **C′** or **C″** would suppress such side reactions. Indeed, this was achieved by the addition of allyltrimethylsilane. Thus, the treatment of **3i** or **3l** in the presence of allyltrimethylsilane (10 equiv) by method A gave the corresponding *p*-quinones **10b** and **10e** in 63% and 75% yields, respectively (runs 9 and 12, Table 2). Similarly, upon addition of allyltrimethylsilane, compounds **3j** and **3k** were converted into the *p*-quinones **10c** and **10d** (runs 10 and 11, Table 2), respectively.

All these results are plausibly rationalized by the following mechanism: At first, the reaction of **3** with TFAA gave the α-acyloxy sulfide **C**. Then, half of **C** was hydrolyzed to give the *p*-quinone **10**, which released the thiol (route a). This thiol reacted with the other half of **C** to give the *p*-dihydroquinone mono(trifluoroacetate) **9** and the disulfide (route b) (Scheme 7). This corresponds to the fact that a 1:1 mixture of the *p*-dihydroquinone **9**

Scheme 6



Scheme 7

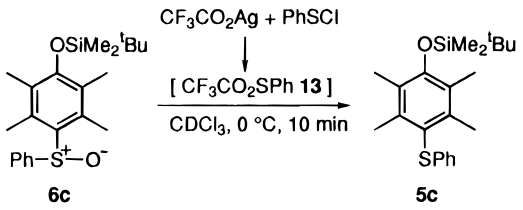


and the *p*-quinone **10** was primarily obtained along with a similar yield of the corresponding disulfide. When allyltrimethylsilane was added, it quickly attacked the sulfur atom of the intermediate **C**, giving **9** and allyl phenyl sulfide. The *p*-dihydroquinone **9** was readily oxidized to the *p*-quinone **10** by alkaline workup or MnO_2 treatment.

Thus, a mild and effective preparation of *p*-quinones **10** having a variety of functional groups is available by choosing the reaction conditions. Generally, method A gives slightly better yields of **10** than method B; however, it is not sufficient for the substrates having electron-withdrawing groups. In such cases, method B is recommended. If the reaction using only TFAA was complicated due to side reactions, the addition of allyltrimethylsilane should be tried as the second choice.

Synthesis of Protected *p*-Dihydroquinones. Next, the above method was extended to the phenol ethers **6**.

Scheme 8



If the reaction of **6** with trifluoroacetic anhydride would cause a similar Pummerer-type reaction, an electrophilic oxonium intermediate **D** would be formed, which would be predominantly attacked by the counteranion at the sulfur atom to selectively give the protected dihydroquinones **14**. For success of this reaction, the OR^1 group must be efficiently electron-donating and the $O-R^1$ bond must be stable in the intermediate **D**.

Although the reaction of the acetate **6a** did not proceed at room temperature even for 2 d (run 1, Table 3), a similar reaction of the methyl ether **6b** with TFAA in $CDCl_3$ was completed at 0 °C within 30 min to give the desired trifluoroacetoxy derivative **14b** (51% yield) accompanied by the reduced product **5b** (48% yield) (run 2, Table 3) [in this reaction, $CHCl_3$ and $CDCl_3$ gave better results than CH_2Cl_2 used in preparation of *p*-quinones]. The treatment of the *tert*-butyldimethylsilyl ether **6c** also gave the corresponding *p*-dihydroquinone derivative **14c** in better yield (58%) (run 3, Table 3). Although the use of the electron-donating (*p*-methoxyphenyl)sulfinyl derivative **6f** instead of **6c** increased the yield of **14c** to 73% yield (run 6, Table 3), we could not depress the formation of **5** by changing the silyl groups (for example, runs 4 and 5, Table 3) and the R^2 group (for example, runs 7−9, Table 3). The use of the *p*-methylsulfinyl derivative **6j** provided a normal Pummerer rearrangement product, the *p*-[[(trifluoroacetoxy)methyl]thio]phenyl silyl ether in 94% yield (run 10, Table 3).

Since it is thought that the attack of the trifluoroacetoxy anion on the sulfur atom of the intermediate **D** gives **14** and the sulfenyl trifluoroacetate **13** [indeed, the addition of 3 equiv of trifluoroacetic acid slightly improved the yield of **14c** (run 11, Table 3)[29]], formation of **5** must be due to the reaction of **13** with unreacted **6**. This was confirmed by the fact that treatment of **6c** with **13** *in situ* prepared from silver trifluoroacetate and phenylsulfenyl chloride[30] at 0 °C immediately gave **5c** in 70% yield (Scheme 8).[31] Therefore, use of an additive that decomposes **13** or attacks the sulfur atom of **D** instead of CF_3COO^- should resolve this problem. The addition of thiophilic compounds such as thiols and $P(OMe)_3$ did not work well for this purpose (runs 12−14, Table 3).

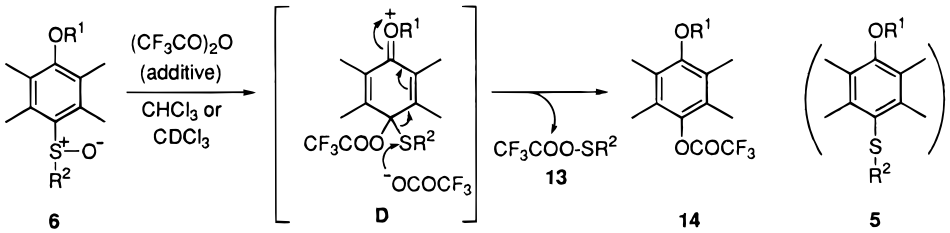
However, alkenes such as styrene, 3,3-dimethylbut-1-ene, and allyltrimethylsilane efficiently trapped **13** to dramatically increase the yield of **14c** (runs 1−3, Table 4).[31c] Although about 10−20% of the trifluoroacetate **14** decomposed during purification by flash column chromatography on SiO_2, we could obtain an excellent yield of the corresponding acetate by the hydrolysis of **14**

(29) Hamel, P.; Girard, Y.; Atkinson, J. G. *J. Org. Chem.* **1992**, *57*, 2694.

(30) Havlik, A. J.; Kharasch, N. *J. Am. Chem. Soc.* **1956**, *78*, 1207.

(31) The compound **13** and its decomposition product, PhSS(O)Ph, seem to be the plausible reductive species, although their reduction mechanisms have not been cleared yet. See: (a) Bell, P. A.; Hogg, D. R.; Robertson, A. *J. Chem. Soc., Perkin Trans. 1* **1978**, 1246. (b) Block, E.; O'Connor, J. *J. Am. Chem. Soc.* **1974**, *96*, 3921. (c) Morishita, T.; Furukawa, N.; Oae, S. *Tetrahedron* **1981**, *37*, 3115.

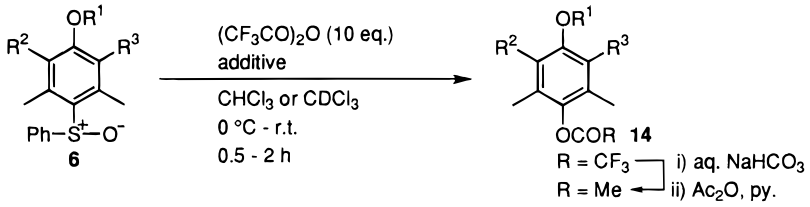
Table 3. Pummerer-Type Reaction of the *p*-Sulfinylphenol Derivatives 6[a]



run	substrate **6**			additive (equiv)	reaction condns	product[b] (%)			
		R^1 =	R^2 =			**14**		**5**	
1	**a**	Ac	Ph	none	rt, 2 d	**a**	N.D.	**a**	ca. 10
2	**b**	Me	Ph	none	0 °C, 30 min	**b**	51 (50[c])	**b**	48 (42[c])
3	**c**	$SiMe_2{}^tBu$	Ph	none	0 °C, 30 min	**c**	58	**c**	39
4	**d**	Si^iPr_3	Ph	none	0 °C, 30 min	**d**	62	**d**	37
5	**e**	$SiPh_2{}^tBu$	Ph	none	0 °C, 30 min	**e**	51	**e**	48
6	**f**	$SiMe_2{}^tBu$	C_6H_4-*p*-OMe	none	0 °C, 2 h	**c**	73 (66[c])	**f**	27 (25[c])
7	**g**	$SiMe_2{}^tBu$	C_6H_4-*p*-F	none	0 °C, 30 min	**c**	60	**g**	40
8	**h**	$SiMe_2{}^tBu$	C_6H_4-*p*-NO_2	none	rt, 1 d	**c**	20	**h**	ca. 20
9	**i**	$SiMe_2{}^tBu$	^{t}Bu	none	0 °C, 10 min	**c**	60	**i**	ca. 10
10	**j**	$SiMe_2{}^tBu$	Me	none	0 °C, 10 min	**c**	trace[d]	**j**	trace
11	**c**	$SiMe_2{}^tBu$	Ph	CF_3COOH (3)	0 °C, 1 h	**c**	68	**c**	28
12	**c**	$SiMe_2{}^tBu$	Ph	PhSH (2)	0 °C, 30 min	**c**	15	**c**	84
13	**c**	$SiMe_2{}^tBu$	Ph	*o*-$HSC_6H_4CO_2H$ (1)	0 °C, 2 h	**c**	54	**c**	44
14	**c**	$SiMe_2{}^tBu$	Ph	$P(OMe)_3$ (1)	0 °C, 2 h	**c**	51	**c**	40

[a] 10 equiv of $(CF_3CO)_2O$ was used for runs 1 and 11−14, and 5 equiv of $(CF_3CO)_2O$ was used for runs 2-10. [b] Yield was estimated by ^{1}H NMR analysis run in $CDCl_3$ with an internal standard ($Cl_2CHCHCl_2$) unless otherwise noted. [c] The same reaction run in $CHCl_3$ and isolated yield by flash column chromatography on SiO_2 is shown. [d] The corresponding *p*-[[(trifluoroacetoxy)methyl]thio]phenyl silyl ether was obtained in 94% yield.

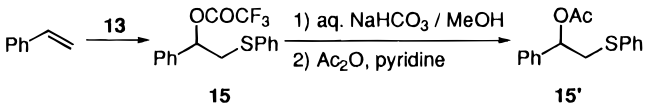
Table 4. Pummerer-Type Reaction of 6 Having Various Functional Groups in the Presence of Additives



run	substrate **6**				additive (equiv)	product **14**	yield[a] (%)
		R^1 =	R^2 =	R^3 =			
1	**c**	$SiMe_2{}^tBu$	Me	Me	styrene (3)	**c**	96 (98,[b] 79[c])
2	**c**	$SiMe_2{}^tBu$	Me	Me	^{t}Bu-CH=CH_2 (3)	**c**	90 (98[b])
3	**c**	$SiMe_2{}^tBu$	Me	Me	allyltrimethylsilane (3)	**c**	76
4	**c**	$SiMe_2{}^tBu$	Me	Me	$PhI(OCOCF_3)_2$ (1)	**c**	97[b]
5	**b**	Me	Me	Me	styrene (3)	**b**	84[c] (98[b])
6	**k**	$SiMe_2{}^tBu$	Me	allyl	styrene (3)	**f**	95
7	**l**	$SiMe_2{}^tBu$	Me	$(CH_2)_3OSiMe_2{}^tBu$	styrene (3)	**g**	86
8	**m**	$SiMe_2{}^tBu$	Me	$(CH_2)_3OAc$	styrene (3)	**h**	98
9	**n**	$SiMe_2{}^tBu$	Me	$(CH_2)_2CHO$	styrene (3)	**i**	62
10	**o**	$SiMe_2{}^tBu$	Me	$(CH_2)_3OH$	styrene (3)	**h**[d]	98
11	**p**	$SiMe_2{}^tBu$	Pr	Pr	styrene (3)	**j**	60
12	**q**	$SiMe_2{}^tBu$	allyl	allyl	styrene (3)	**k**	63

[a] Isolated yield of the corresponding acetate. [b] Yield of trifluoroacetate estimated by ^{1}H NMR analysis run in $CDCl_3$ with an internal standard ($Cl_2CHCHCl_2$). [c] Isolated yield of trifluoroacetate by flash column chromatography on SiO_2. [d] The hydroxyl group was acetylated during the reaction.

Scheme 9



followed by acetylation (see the Experimental Section). After this exchange treatment, 1-phenyl-2-(phenylsulfenyl)ethyl acetate **15′** was also obtained in 87% yield, which supports the trapping of **13** by styrene (Scheme 9). The use of $PhI(OCOCF_3)_2$ to oxidatively decompose **13** and/or regenerate **6** from **5** also increased the yield of **14c** to 97% (run 4, Table 4), but it was not useful for **6** having other functional groups (*vide infra*). It was thought that the trapping with styrene was the best method for this *p*-dihydroquinone preparation, considering the easy handling and the low cost of the reagent. Similarly, the methyl ether **6b** was converted to the corresponding **14b** in high yield, although it took 15 h (run 5, Table 4).

Next, we examined this method on silyl ethers **6k**−**n,p,q** having allyl, (*tert*-butyldimethylsilyl)oxy, ester, and formyl groups to find that the corresponding dihydroquinones **14f**−**k** were obtained in good to excellent yields without decomposition of the functional groups (runs 6−9, 11, 12). The hydroxy group of **6o** also did not disturb the reaction, and the product **14h** was almost quantitatively obtained (run 10, Table 4).[32]

Conclusions

In conclusion, we have succeeded in the novel direct *ipso*-substitution of the sulfinyl group of *p*-sulfinylphenol derivatives **3** and **6** by oxygen functional groups on aromatic rings. This method can offer the selective preparation of *p*-quinones **10** and *p*-dihydroquinones **14** and also features very mild reaction conditions, simple operation, and compatibility with various functional groups including carbonyl groups. The formation of the *p*-dihydroquinones **14**, whose two hydroxy groups are protected by different protective groups, should be of use in the various fields of organic synthesis. Extension of the present method for the synthesis of *peri*-hydroxy polycyclic aromatic natural products is now in progress.[32]

Experimental Section

All melting points are uncorrected. Infrared (IR) absorption spectra were recorded as a KBr pellet. ^{1}H NMR spectra were measured in $CDCl_3$ on 200, 250, and 270 MHz spectrometers with $SiMe_4$ or $CHCl_3$ (δ 7.26) as internal standards. E. Merck silica gel 60 (0.063−0.200 nm, 70−230 mesh ASTM), Fuji Silysia Chemical silica gel BW-300, and E. Merck precoated TLC plates silica gel 60 F_{254} were used for column chromatography, flash column chromatography, and preparative TLC, respectively. Anhydrous $CHCl_3$ (99.5%, stabilized with 150 ppm of amylene, water ≤0.003%, Kanto Chemical Co.) and $CDCl_3$ (99.8%D, Euriso-top) were used as such. Anhydrous CH_2Cl_2 was distilled from P_2O_5.

The *p*-Sulfinylphenols 3a−d,f,h were prepared by direct *p*-sulfinylation of the corresponding phenols similarly to the reported method.[19a] The corresponding sulfinyl chlorides except for PhSOCl were prepared according to the reported method.[33]

2,3,5,6-Tetramethyl-4-(phenylsulfinyl)phenol (3a). Typical Procedure. To an ice-cooled suspension of $PhSO_2Na\cdot 2H_2O$ (1.34 g, 6.7 mmol) in dry benzene (50 mL) was added thionyl chloride (4.5 mL, 61 mmol). After being stirred for 10 min, the reaction mixture was warmed to room temperature and stirred for 12 h. The reaction mixture was concentrated in vacuo to give crude PhSOCl. To a solution of 2,3,5,6-tetramethylphenol (450 mg, 3.0 mmol) in dry CH_2Cl_2 (6 mL) was added $AlCl_3$ (400 mg, 3.0 mmol) at 0 °C. After a few minutes, a solution of crude PhSOCl in dry CH_2Cl_2 (10 mL) was added slowly at 0 °C. After being stirred for 30 min, the reaction mixture was poured into ice−water and then extracted with CH_2Cl_2. The organic layer was washed with brine, dried with Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography (CH_2Cl_2 → CH_2Cl_2−MeOH 50:1 → CH_2Cl_2−MeOH 20:1) to give **3a** (576 mg, 70%) as white crystals: mp 142−148 °C dec (benzene−hexane); IR 3600−2800 br, 1582, 1561, 1080 cm^{-1}; ^{1}H NMR δ 2.10 (s, 6H), 2.28 (s, 6H), 7.39 (br s, 5H). Anal. Calcd for $C_{16}H_{18}O_2S$: C, 70.04; H, 6.61; S, 11.68. Found: C, 70.01; H, 6.53; S, 11.58.

4-[(4-Methoxyphenyl)sulfinyl]-2,3,5,6-tetramethylphenol (3b): 40% from 2,3,5,6-tetramethylphenol; white crystals; mp 134−136 °C (CH_2Cl_2−hexane); IR 3500−3000 br, 1593, 1559, 1084 cm^{-1}; ^{1}H NMR δ 2.12 (s, 6H), 2.33 (s, 6H), 3.82 (s, 3H), 5.75 (s, 1H), 6.93 (d, J = 9.0 Hz, 2H), 7.29 (d, J = 9.0 Hz, 2H); HRMS calcd for $C_{17}H_{20}O_3S$ 304.1133, found 304.1121. Anal. Calcd for $C_{17}H_{20}O_3S$: C, 67.08; H, 6.62; S, 10.53. Found: C, 66.68; H, 6.47; S, 10.60.

2,3,5,6-Tetramethyl-4-[(4-methylphenyl)sulfinyl]phenol (3c): 89% from 2,3,5,6-tetramethylphenol; white crystals; mp 144−146 °C (CH_2Cl_2−hexane); IR 3500−3000 br, 1559, 1080, 1021 cm^{-1}; ^{1}H NMR δ 2.11 (s, 6H), 2.30 (s, 6H), 2.37 (s, 3H), 5.29 (s, 1H), 7.22−7.28 (m, 4H). Anal. Calcd for $C_{17}H_{20}O_2S$: C, 70.80; H, 6.99; S, 11.12. Found: C, 70.68; H, 6.87; S, 11.00.

4-[(4-Chlorophenyl)sulfinyl]-2,3,5,6-tetramethylphenol (3d): 15% from 2,3,5,6-tetramethylphenol; white crystals; mp 148−150 °C (CH_2Cl_2−hexane); IR 3300−3000 br, 1557, 1075, 1022 cm^{-1}; ^{1}H NMR δ 2.14 (s, 6H), 2.36 (s, 6H), 5.27 (s, 1H), 7.30−7.41 (m, 4H); HRMS calcd for $C_{16}H_{17}O_2S^{35}Cl$ 308.0638, found 308.0731. Anal. Calcd for $C_{16}H_{17}O_2SCl$: C, 62.23; H, 5.55. Found: C, 61.91; H, 5.51.

2,3,5,6-Tetramethyl-4-(methylsulfinyl)phenol (3f): 74% from 2,3,5,6-tetramethylphenol; white crystals; mp 148−150 °C (CH_2Cl_2−hexane); IR 3300−3000 br, 1557, 1107, 1013 cm^{-1}; ^{1}H NMR δ 2.15 (s, 6H), 2.53 (s, 6H), 2.87 (s, 3H), 5.30 (s, 1H). Anal. Calcd for $C_{11}H_{16}O_2S$: C, 62.23; H, 7.60; S, 15.10. Found: C, 62.07; H, 7.46; S, 15.10.

2,3,5,6-Tetramethyl-4-[(4-nitrophenyl)sulfinyl]phenol (3h): 10% from 2,3,5,6-tetramethylphenol; pale yellow crystals; mp 158−160 °C (CH_2Cl_2−hexane); IR 3300−3000 br, 1603, 1582, 1557, 1101, 1011 cm^{-1}; ^{1}H NMR ($CDCl_3$−CD_3OD) δ 2.16 (s, 6H), 2.35 (s, 6H), 7.58 (d, J = 9.0 Hz, 2H), 8.29 (d, J = 9.0 Hz, 2H); HRMS calcd for $C_{16}H_{17}NO_4S$ 319.0878, found 319.0871.

The *p*-sulfinylphenols (3g,i−l,n−q) were prepared from the corresponding *p*-thiocyanatophenols (**4**)[22] by stepwise *p*-sulfinylation.

3,5-Dimethyl-4-(phenylsulfinyl)phenol (3i). Typical Procedure. Under a nitrogen atmosphere, a solution of 3,5-dimethyl-4-thiocyanatophenol (**4i**) (54 mg, 0.30 mmol) and *O*-methyl-*O*-(*tert*-butyldimethylsilyl)ketene acetal (169 mg, 0.90 mmol) in dry MeCN (3 mL) was stirred at room temperature for 2 h.[25] The reaction mixture was concentrated in vacuo to give the silyl ether **7i**, which was dissolved in dry THF (3 mL), and the solution was cooled to −50 °C. To the solution was added PhMgBr (3.0 M Et_2O solution, 0.30 mL, 0.90 mmol) slowly, and the stirring was continued for 1 h. The reaction mixture was quenched with saturated aqueous NH_4Cl at the same temperature and extracted with AcOEt. The organic layer was washed with brine, dried with Na_2SO_4, and concentrated in vacuo. The residue was dissolved in THF (2 mL) and H_2O (0.02 mL), to which was added Bu_4NF (1.0 M THF solution, 0.06 mL, 0.06 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 3.5 h, quenched with saturated aqueous NH_4Cl, and extracted with AcOEt. The organic layer was washed with brine, dried with Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography (hexane−AcOEt 3:1) to give the *p*-sulfenylphenol **2i** (56 mg, 81% from **4i**). **2i**: white crystals; mp 109−110 °C (AcOEt−hexane); IR 3700−3100 br, 1584 cm^{-1}; ^{1}H NMR δ 2.38 (s, 6H), 4.97 (s, 1H), 6.68 (s, 2H), 6.88−7.17 (m, 5H). Anal. Calcd for $C_{14}H_{14}OS$: C, 73.01; H, 6.13; S, 13.92. Found: C, 72.84; H, 6.07; S, 13.92.

Under a nitrogen atmosphere, *m*-CPBA (109 mg, 80% purity, 0.50 mmol) was added to a solution of **2i** (116 mg, 0.50 mmol) in dry CH_2Cl_2 (2.5 mL) at −50 °C. The reaction mixture was stirred at −50 → −30 °C for 2 h. A saturated aqueous solution of $Na_2S_2O_3$ (3 mL) was added, and the whole mixture was stirred vigorously for 5 min. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2. The combined organic layer was washed with saturated aqueous $NaHCO_3$, dried with Na_2SO_4, and concentrated in vacuo. The residue was washed with Et_2O to give **3i** (107 mg, 80%) as white crystals: mp 154−155 °C (CH_2Cl_2−hexane); IR 3300−2500 br, 1578, 1082, 1067 cm^{-1}; ^{1}H NMR ($CDCl_3$−CD_3OD) δ 2.35 (s, 6H), 6.54 (s, 2H), 7.26−7.53 (m, 5H). Anal. Calcd for $C_{14}H_{14}O_2S$: C, 68.26; H, 5.73; S, 13.02. Found: C, 68.22; H, 5.72; S, 12.92.

2,3-Bis(ethoxycarbonyl)-4-(phenylsulfinyl)naphthol (3o). Similar to the preparation of **3i**, crude **7o**, prepared from **4o** (87 mg, 0.25 mmol) and *O*-methyl-*O*-(*tert*-butyldimethylsilyl)ketene acetal (119 mg, 0.63 mmol), was treated with PhMgBr (3.0 M Et_2O solution, 0.30 mL, 0.90 mmol) at −50 °C for 1 h and then with Bu_4NF (1.0 M THF solution, 0.06 mL, 0.06 mmol) at −30 °C for 5 h. Usual workup and purification by column chromatography (hexane−AcOEt 10:1) gave **2o** (56 mg, 57% from **7o**). **2o**: white crystals; mp 126−127 °C

(32) Very recently, we have applied this transformation to a novel and efficient synthesis of *peri*-hydroxydihydroquinone derivatives. Kita, Y.; Takeda, Y.; Iio, K.; Yokogawa, K.; Takahashi, K.; Akai, S. *Tetrahedron Lett.* **1996**, *37*, 7545.

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(hexane−AcOEt); IR 3500−2500 br, 1659, 1619 cm^{-1}; ^1H NMR δ 1.22 (t, J = 7.5 Hz, 3H), 1.42 (t, J = 7.5 Hz, 3H), 4.36 (q, J = 7.5 Hz, 2H), 4.46 (q, J = 7.5 Hz, 2H), 7.05−7.15 (m, 5H), 7.57−7.64 (m, 2H), 8.35−8.51 (m, 2H). Anal. Calcd for $C_{22}H_{20}O_5S$: C, 66.65; H, 5.08; S, 8.09. Found: C, 66.54; H, 5.10; S, 8.04.

The product **2o** (100 mg, 0.25 mmol) was treated with *m*-CPBA (56 mg, 80% purity, 0.25 mmol) as shown above, and the crude product was purified by column chromatography (hexane−AcOEt 3:1) to give **3o** (83 mg, 80%) as yellow crystals: mp 161−164 °C (CH_2Cl_2−hexane); IR 1734, 1663, 1619, 1580, 1084, 1049 cm^{-1}; ^1H NMR δ 1.43 (t, J = 7.0 Hz, 3H), 1.45 (t, J = 7.0 Hz, 3H), 4.42−4.54 (m, 4H), 7.31−7.74 (m, 7H), 8.42−8.45 (m, 1H), 8.57−8.60 (m, 1H), 13.12 (s, 1H). Anal. Calcd for $C_{22}H_{20}O_6S$: C, 64.06; H, 4.89; S, 7.77. Found: C, 63.83; H, 4.93; S, 7.80.

4-(*tert*-Butylsulfinyl)-2,3,5,6-tetramethylphenol (3g): 65% from the corresponding **4**; white crystals; mp 158−159 °C (CH_2Cl_2); IR 3300−2900 br, 1555, 1005; ^1H NMR δ 1.26 (s, 9H), 2.14 (s, 3H), 2.16 (s, 3H), 2.36 (s, 3H), 2.66 (s, 3H), 5.19 (s, 1H). Anal. Calcd for $C_{14}H_{22}O_2S$: C, 66.10; H, 8.72; S, 12.60. Found: C, 66.03; H, 8.61; S, 12.55.

2,3,5-Trimethyl-4-(phenylsulfinyl)phenol (3j): 63% from the corresponding **4**; white crystals; mp 129−130 °C (CH_2Cl_2−hexane); IR 3300−2900 br, 1582 cm^{-1}; ^1H NMR δ 2.10 (s, 3H), 2.33 (s, 3H), 2.37 (s, 3H), 5.76 (s, 1H), 6.49 (s, 1H), 7.38−7.44 (m, 5H). Anal. Calcd for $C_{15}H_{16}O_2S$: C, 69.20; H, 6.19. Found: C, 68.97; H, 6.23.

2-Acetyl-3,5,6-trimethyl-4-(phenylsulfinyl)phenol (3k): 45% from the corresponding **4**; white crystals; mp 129−131 °C (CH_2Cl_2−hexane); IR 3300−2750 br, 1698, 1620 cm^{-1}; ^1H NMR δ 2.15 (s, 3H), 2.39 (s, 3H), 2.61 (s, 3H), 2.67 (s, 3H), 7.36−7.46 (m, 5H), 11.87 (s, 1H). Anal. Calcd for $C_{17}H_{18}O_3S$: C, 67.52; H, 6.00; S, 10.60. Found: C, 67.24; H, 5.97; S, 10.54.

2-Allyl-3,5,6-trimethyl-4-(phenylsulfinyl)phenol (3l): 70% from the corresponding **4**; white crystals; mp 99−100 °C (CH_2Cl_2−hexane); IR 3400−2900 br, 1636, 1582, 1557, 1080 cm^{-1}; ^1H NMR δ 2.14 (s, 3H), 2.36 (s, 3H), 2.39 (s, 3H), 3.42 (d, J = 5.5 Hz, 2H), 4.99 (dd, J = 16.0, 1.5 Hz, 1H), 5.09 (dd, J = 10.5, 1.5 Hz, 1H), 5.92 (ddt, J = 16.0, 10.5, 5.5 Hz, 1H), 7.33−7.46 (m, 5H). Anal. Calcd for $C_{18}H_{20}O_2S$: C, 71.97; H, 6.71; S, 10.67. Found: C, 71.91; H, 6.75; S, 10.56.

2-(Ethoxycarbonyl)-3-methyl-4-(phenylsulfinyl)naphthol (3n): 46% from the corresponding **4**; white crystals; mp 161−164 °C (CH_2Cl_2−hexane); IR 1736, 1669, 1597 cm^{-1}; ^1H NMR δ 1.48 (t, J = 7.0 Hz, 3H), 2.99 (s, 3H), 4.53 (q, J = 7.0 Hz, 2H), 7.31−7.54 (m, 7H), 8.43 (d, J = 7.5 Hz, 1H), 8.55 (d, J = 8.5 Hz, 1H), 13.05 (s, 1H). Anal. Calcd for $C_{20}H_{18}O_4S$: C, 67.78; H, 5.12; S, 9.05. Found: C, 67.68; H, 5.15; S, 9.05.

2-(*N*,*N*-Diethylcarbamoyl)-3-methyl-4-(phenylsulfinyl)naphthol (3p): 77% from the corresponding **4**; white crystals mp 154−156 °C (CH_2Cl_2−hexane); IR 1617, 1605, 1561, 1082, 1042 cm^{-1}; ^1H NMR δ 1.09−1.28 (m, 6H), 2.64 (s, 3H), 3.20−3.80 (s, 4H), 7.29−7.46 (m, 7H), 8.12 (d, J = 8.0 Hz, 1H), 8.37 (brs, 1H), 8.46 (d, J = 8.0 Hz, 1H); HRMS calcd for $C_{22}H_{23}NO_3S$ 381.1398, found 381.1386.

2,3-Bis(*N*,*N*-diethylcarbamoyl)-4-(phenylsulfinyl)naphthol (3q): 41% from the corresponding **4**; white crystals; mp 96−98 °C (hexane−CH_2Cl_2); IR 3200−2400 br, 1636, 1601, 1559, 1082, 1046 cm^{-1}; ^1H NMR δ 1.06−1.36 (m, 12H), 3.15−3.92 (m, 8H), 7.27−7.43 (m, 5H), 7.84 (d, J = 7.0 Hz, 2H), 8.07 (d, J = 8.0 Hz, 1H), 8.53 (d, J = 8.0 Hz, 1H); HRMS calcd for $C_{26}H_{30}N_2O_4S$ 466.1926, found 466.1928.

4-[(4-Fluorophenyl)sulfinyl]-2,3,5,6-tetramethylphenol (3e). Typical Procedure for Desilylation of 6. To an ice-cooled solution of **6g** (45 mg, 0.11 mmol) (whose preparation is shown below) in THF (2.5 mL) and H_2O (0.5 mL) was added Bu_4NF (1.0 M THF solution, 0.050 mL, 0.050 mmol), and the reaction mixture was stirred for 1 h. The reaction mixture was poured into saturated aqueous NH_4Cl and extracted with CH_2Cl_2. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2. The combined organic layer was washed with brine, dried with Na_2SO_4, and concentrated in vacuo. The residue was purified by preparative TLC (CH_2Cl_2−MeOH 50:1) to give **3e** (31 mg, 98%) as white crystals: mp 131−133 °C (CH_2Cl_2−hexane); IR 3700−3000 br, 1588, 1080 cm^{-1}; ^1H NMR δ 2.15 (s, 6H), 2.36 (s, 6H), 5.25 (s, 1H), 7.06−7.16 (m, 2H), 7.33−7.40 (m, 2H). Anal. Calcd for $C_{16}H_{17}FO_2S$: C, 65.73; H, 5.86. Found: C, 65.70; H, 5.87.

2-(3-Hydroxypropyl)-3,5,6-trimethyl-4-(phenylsulfinyl)phenol (3m): quant. from the corresponding **6l**; white crystals; mp 146−148 °C (CH_2Cl_2−hexane); IR 3500−3000 br, 1555, 1080 cm^{-1}; ^1H NMR δ 1.76−1.82 (m, 2H), 2.15 (s, 3H), 2.34 (s, 3H), 2.37 (s, 3H), 2.77 (t, J = 6.5 Hz, 2H), 3.45 (br s, 1H), 3.53−3.58 (m, 2H), 7.35−7.43 (m, 5H), 8.28 (s, 1H). Anal. Calcd for $C_{18}H_{22}O_3S$: C, 67.89; H, 6.96. Found: C, 67.57; H, 6.95.

Reaction of 4i with PhMgBr. Under a nitrogen atmosphere, to a solution of **4i** (179 mg, 1.0 mmol) in dry THF (10 mL) was added PhMgBr (3.0 M Et_2O solution, 1.0 mL, 3.0 mmol) slowly at −50 °C, and the stirring was continued for 4 h. The reaction mixture was quenched with saturated aqueous NH_4Cl at the same temperature and extracted with AcOEt. The organic layer was washed with brine, dried with Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography (CH_2Cl_2 → CH_2Cl_2−MeOH 50:1 → CH_2Cl_2−MeOH 20:1) to give **2i** (120 mg, 52%) and **8i** (64 mg, 42%). **8i**: pale yellow crystals; mp 187−189 °C (benzene); IR 3333, 1586, 1306, 1161 cm^{-1}; ^1H NMR δ 2.20 (s, 12H), 4.92 (s, 2H), 6.50 (s, 4H). Anal. Calcd for $C_{16}H_{18}O_2S_2$: C, 62.71; H, 5.92; S, 20.92. Found: C, 62.62; H, 5.85; S, 20.82.

2,3,5,6-Tetramethyl-4-(phenylsulfinyl)phenyl Acetate (6a). 6a was prepared by the acetylation (Ac_2O, pyridine) of **3a**. **6a**: quant.; white crystals; mp 164−165 °C (hexane); IR 1755, 1200, 1080, 1044 cm^{-1}; ^1H NMR δ 2.05 (s, 6H), 2.37 (s, 6H), 2.40 (s, 3H), 7.42 (brs, 5H). Anal. Calcd for $C_{18}H_{20}O_3S$: C, 68.33; H, 6.37; S, 10.13. Found: C, 68.34; H, 6.33; S, 10.24.

Methyl 2,3,5,6-Tetramethyl-4-(phenylsulfinyl)phenyl Ether (6b). 6b was prepared by the methylation (MeI and K_2CO_3) of **3a**. **6b**: quant.; white crystals; mp 133−135 °C (hexane); IR 1100, 1082, 1044 cm^{-1}; ^1H NMR δ 2.19 (s, 6H), 2.37 (s, 6H), 3.66 (s, 3H), 7.41 (brs, 5H). Anal. Calcd for $C_{17}H_{20}O_2S$: C, 70.79; H, 6.99; S, 11.12. Found: C, 70.68; H, 7.06; S, 10.94.

***tert*-Butyldimethylsilyl 2,3,5,6-Tetramethyl-4-(phenylsulfinyl)phenyl Ether (6c). Typical Procedure for Preparation of the Silyl Ethers 6c−f,h,j,p from 3.** Under a nitrogen atmosphere, imidazole (0.26 g, 3.8 mmol) and $^tBuMe_2SiCl$ (0.41 g, 2.7 mmol) were added to an ice-cooled solution of **3a** (0.50 g, 1.8 mmol) in dry DMF (6 mL), and the reaction mixture was stirred at room temperature for 30 h. Ether (30 mL) was added, and the whole mixture was washed with water (30 mL × 2), dried with $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography (hexane−AcOEt 5:1) to give **6c** (0.69 g, 97%) as white crystals: mp 125−127 °C (hexane); IR 1551, 1109, 1082, 1046 cm^{-1}; ^1H NMR δ 0.14 (s, 6H), 1.05 (s, 9H), 2.10 (s, 6H), 2.34 (s, 6H), 7.40 (brs, 5H). Anal. Calcd for $C_{22}H_{32}O_2SSi$: C, 67.99; H, 8.30; S, 8.25. Found: C, 67.96; H, 8.20; S, 8.17.

Triisopropylsilyl 2,3,5,6-tetramethyl-4-(phenylsulfinyl)-phenyl ether (6d): 70% from **3a**; white crystals; mp 148−150 °C (hexane); IR 1551, 1300, 1115, 1044 cm^{-1}; ^1H NMR δ 1.10 (d, J = 6.0 Hz, 18H), 1.11 (s, 9H), 1.17−1.40 (m, 3H), 2.14 (s, 6H), 2.34 (s, 6H), 7.35−7.40 (m, 5H). Anal. Calcd for $C_{25}H_{38}O_2SSi$: C, 69.71; H, 8.89; S, 7.44. Found: C, 69.56; H, 8.86; S, 7.33.

***tert*-Butyldiphenylsilyl 2,3,5,6-tetramethyl-4-(phenylsulfinyl)phenyl ether (6e):** 94% from **3a**; white crystals; mp 161−163 °C (hexane); IR 1298, 1113, 1044 cm^{-1}; ^1H NMR δ 1.12 (s, 9H), 1.90 (s, 6H), 2.25 (s, 6H), 7.30−7.46 (m, 11H), 7.62−7.72 (m, 4H). Anal. Calcd for $C_{32}H_{36}O_2SSi$: C, 74.95; H, 7.08; S, 6.25. Found: C, 75.16; H, 7.24; S, 6.38.

***tert*-Butyldimethylsilyl 4-[(4-methoxyphenyl)sulfinyl]-2,3,5,6-tetramethylphenyl ether (6f):** quant. from **3b**; white crystals; mp 142−144 °C (hexane); IR 1593, 1495, 1109, 1084, 1044 cm^{-1}; ^1H NMR δ 0.14 (s, 6H), 1.05 (s, 9H), 2.10 (s, 6H), 2.35 (s, 6H), 3.83 (s, 3H), 6.93 (d, J = 8.5 Hz, 2H), 7.30 (d, J = 8.5 Hz, 2H). Anal. Calcd for $C_{23}H_{34}O_3SSi$: C, 65.98; H, 8.19; S, 7.66. Found: C, 65.80; H, 8.17; S, 7.63.

***tert*-Butyldimethylsilyl 2,3,5,6-tetramethyl-4-[(4-nitrophenyl)sulfinyl]phenyl ether (6h):** 41% from **3h**; pale yellow crystals; mp 136−138 °C (hexane); IR 1526, 1347, 1109, 1011 cm^{-1}; ^1H NMR δ 0.15 (s, 6H), 1.05 (s, 9H), 2.11 (s, 6H),

2.34 (s, 6H), 7.59 (d, J = 9.0 Hz, 2H), 8.27 (d, J = 9.0 Hz, 2 H). Anal. Calcd for $C_{22}H_{31}NO_4SSi$: C, 60.94; H, 7.20; N, 3.23; S, 7.39. Found: C, 60.73; H, 7.06; N, 3.22; S, 7.32.

***tert*-Butyldimethylsilyl 2,3,5,6-tetramethyl-4-(methylsulfinyl)phenyl ether (6j):** 25% from **3f**; white crystals; mp 81−84 °C (hexane); IR 1551, 1107, 1057 cm^{-1}; ^1H NMR δ 0.13 (s, 6H), 1.04 (s, 9H), 2.11 (s, 6H), 2.51 (s, 6H), 2.88 (s, 3H). Anal. Calcd for $C_{17}H_{30}O_2SSi$: C, 62.52; H, 9.26; S, 9.82. Found: C, 62.33; H, 9.27; S, 9.75.

***tert*-Butyldimethylsilyl 3,5-Dimethyl-2,6-dipropyl-4-(phenylsulfinyl)phenyl Ether (6p). 6p** was prepared by direct sulfinylation (60%) of 3,5-dimethyl-2,6-dipropylphenol and silylation (quant.) as a colorless oil: IR 1581, 1545, 1296, 1117, 1046 cm^{-1}; ^1H NMR δ 0.19 (s, 3H), 0.20 (s, 3H), 0.87 (t, J = 7.5 Hz, 6H), 0.99 (s, 9H), 1.38 (sext., J = 7.5 Hz, 4H), 2.37 (s, 6H), 2.57 (t, J = 7.5 Hz, 4H), 7.34−7.40 (m, 5H); HRMS calcd for $C_{26}H_{40}O_2Si$ 444.2518, found 444.2516.

***tert*-Butyldimethylsilyl 4-[(4-Fluorophenyl)sulfinyl]-2,3,5,6-tetramethylphenyl Ether (6g). Typical Procedure for Preparation of the Silyl Ethers 6g,i,k−o,q.** Similar to the preparation of **6c**, 2,3,5,6-tetramethyl-4-thiocyanatophenol **4** (0.30 g, 1.4 mmol) was stirred with ^{t}BuMe$_2$SiCl (0.40 g, 2.7 mmol) and imidazole (0.20 g, 2.9 mmol) in dry DMF (8 mL) and was worked up to give *tert*-butyldimethylsilyl 2,3,5,6-tetramethyl-4-(thiocyanato)phenyl ether (**7**) (0.40 g, 87%) as white crystals: mp 73−74 °C (hexane); IR 2153, 1552, 1109 cm^{-1}; ^1H NMR δ 0.14 (s, 6H), 1.05 (s, 9H), 2.15 (s, 6H), 2.53 (s, 6H). Anal. Calcd for $C_{17}H_{27}NOSSi$: C, 63.50; H, 8.46; N, 4.36; S, 9.97. Found: C, 63.37; H, 8.41; N, 4.33; S, 9.94.

Under a nitrogen atmosphere, 4-FC_6H_4MgBr (2.0 M Et_2O solution, 1.6 mL, 3.2 mmol) was added to a solution of the above silyl ether (0.30 g, 0.94 mmol) in dry THF (10 mL) at −70 °C, and the reaction mixture was stirred at the same temperature for 20 min. Saturated aqueous NH_4Cl (20 mL) was added, and the mixture was extracted with AcOEt (20 mL × 3). The combined organic layer was washed with brine, dried with Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography (hexane → hexane−AcOEt 50:1) to give the 4-[(4-fluorophenyl)thio]phenyl silyl ether **5** (0.27 g, 69%) as white crystals: mp 86−89 °C (hexane); IR 1590, 1489, 1105, 1011 cm^{-1}; ^1H NMR δ 0.17 (s, 6H), 1.07 (s, 9H), 2.16 (s, 6H), 2.39 (s, 6H), 6.84−6.88 (m, 4H). Anal. Calcd for $C_{22}H_{31}FOSSi$: C, 67.64; H, 8.00. Found: C, 67.83; H, 7.84.

Under a nitrogen atmosphere, *m*-CPBA (11 mg, 80% purity, 0.063 mmol) was added to a solution of the above ether (25 mg, 0.063 mmol) in dry CH_2Cl_2 (6 mL) at −50 °C. The reaction mixture was stirred at −50 → −30 °C for 1.5 h. Saturated aqueous $Na_2S_2O_3$ (5 mL) was added, and the whole mixture was stirred vigorously for 5 min. The organic layer was separated, and the aqueous layer was extracted with AcOEt. The combined organic layer was washed with saturated aqueous $NaHCO_3$, dried with Na_2SO_4, and concentrated in vacuo. The residue was purified by prepared TLC (hexane−AcOEt 4:1) to give **6g** (23 mg, 88%) as white crystals: mp 122−123 °C (hexane); IR 1588, 1549, 1153, 1109, 1080, 1045 cm^{-1}; ^1H NMR δ 0.14 (s, 6H), 1.05 (s, 9H), 2.10 (s, 6H), 2.33 (s, 6H), 7.11 (t-like, J = 9.0 Hz, 2H), 7.37 (dd-like, J = 9.0, 5.0 Hz, 2H). Anal. Calcd for $C_{22}H_{31}FO_2SSi$ C, 64.98; H, 7.68. Found: C, 64.93; H, 7.76.

***tert*-Butyldimethylsilyl 4-(*tert*-butylsulfinyl)-2,3,5,6-tetramethylphenyl ether (6i):** 79% (three steps) from the corresponding **4**; white crystals; mp 95−96 °C (hexane); IR 1549, 1171, 1111, 1048 cm^{-1}; ^1H NMR δ 0.13 (s, 3H), 0.14 (s, 3H), 1.04 (s, 9H), 1.26 (s, 9H), 2.10 (s, 6H), 2.33 (s, 3H), 2.64 (s, 3H). Anal. Calcd for $C_{20}H_{36}O_2SSi$: C, 65.16; H, 9.84; S, 8.70. Found: C, 65.16; H, 9.90; S, 8.66.

2-Allyl-3,5,6-trimethyl-4-(phenylsulfinyl)phenyl *tert*-butyldimethylsilyl ether (6k): 72% (three steps) from the corresponding **4**; a colorless oil; IR 1547, 1102, 1082, 1044 cm^{-1}; ^1H NMR δ 0.17 (s, 6H), 1.02 (s, 9H), 2.10 (s, 3H), 2.32 (s, 3H), 2.38 (s, 3H), 3.41 (d, J = 6.0 Hz, 2H), 4.81 (dd, J = 17.0, 1.5 Hz, 1H), 4.95 (dd, J = 10.0, 1.5 Hz, 1H), 5.77 (ddt, J = 17.0, 10.0, 6.0 Hz, 1H), 7.35−7.43 (m, 5H). Anal. Calcd for $C_{24}H_{34}O_2SSi$: C, 69.51; H, 8.26; S, 7.73. Found: C, 69.78; H, 8.53; S, 7.46.

***tert*-Butyldimethylsilyl 2-[3-(*tert*-Butyldimethylsilyloxy)propyl]-3,5,6-trimethyl-4-(phenylsulfinyl)phenyl Ether (6l).** Similar to the preparation of **6c**, 2-(3-hydroxypropyl)-3,5,6-tetramethyl-4-(thiocyanato)phenol (**4**) was stirred with ^{t}BuMe$_2$SiCl and imidazole in dry DMF and was worked up to give *tert*-butyldimethylsilyl 2-[3-[(*tert*-butyldimethylsilyl)-oxy]propyl]-3,5,6-tetramethyl-4-(thiocyanato)phenyl ether (86%). The silyl ether was treated with PhMgBr followed by *m*-CPBA as shown above to give **6l** (2 steps, 76%) as a colorless oil: IR 1474, 1102, 1048 cm^{-1}; ^1H NMR δ 0.02 (s, 6H), 0.16 (s, 6H), 0.88 (s, 9H), 1.02 (s, 9H), 1.51−1.63 (m, 2H), 2.08 (s, 3H), 2.31 (s, 3H), 2.41 (s, 3H), 2.66 (t, J =8.0 Hz, 2H), 3.59 (t, J = 6.0 Hz, 2H), 7.40 (br s, 5H). Anal. Calcd for $C_{30}H_{50}O_3SSi_2$: C, 65.88; H, 9.21; S, 5.86. Found: C, 65.78; H, 9.20; S, 5.73.

2-(3-Acetoxypropyl)-3,5,6-trimethyl-4-(phenylsulfinyl)-phenyl *tert*-Butyldimethylsilyl Ether (6m). 6m was prepared by the acetylation (Ac_2O, pyridine) of **6o**: 90%; a colorless oil; IR 1740, 1547, 1109, 1082, 1044 cm^{-1}; ^1H NMR δ 0.17 (s, 6H), 1.02 (s, 9H), 1.62−1.77 (m, 2H), 2.02 (s, 3H), 2.08 (s, 3H), 2.33 (s, 3H), 2.39 (s, 3H), 2.66−2.74 (m, 2H), 4.02 (t, J = 6.0 Hz, 2H), 7.38−7.42 (m, 5H). Anal. Calcd for $C_{26}H_{38}O_4SSi$: C, 65.71; H, 8.06; S, 6.75. Found: C, 65.57; H, 7.99; S, 6.62.

***tert*-Butyldimethylsilyl 3,5,6-Trimethyl-2-(3-oxopropyl)-4-(phenylsulfinyl)phenyl Ether (6n). 6n** was prepared from 2-(3-hydroxypropyl)-3,5,6-tetramethyl-4-(thiocyanato)-phenol (**4**) as follows. Tetrahydropyranyl (THP) protection of the primary hydroxy group (97%), silylation of phenolic hydroxy group (86%), Grignard reaction (90%), and removal of THP group (94%) gave *tert*-butyldimethylsilyl 2-(3-hydroxypropyl)-3,5,6-tetramethyl-4-(phenylsulfenyl)phenyl ether. This was subjected to Swern oxidation (quant.) and oxidation with *m*-CPBA (84%) to give **6n**: a colorless oil; IR 1725, 1105, 1082, 1044 cm^{-1}; ^1H NMR δ 0.17 (s, 3H), 0.18 (s, 3H), 1.00 (s, 9H), 2.09 (s, 3H), 2.34 (s, 3H), 2.38 (s, 3H), 2.49−2.54 (m, 2H), 2.94 (t, J = 8.0 Hz, 2H), 7.36−7.44 (m, 5H), 9.75 (s, 1H). Anal. Calcd for $C_{24}H_{34}O_3SSi$: C, 66.93; H, 7.96. Found: C, 66.69; H, 8.10.

***tert*-Butyldimethylsilyl 2-(3-Hydroxypropyl)-3,5,6-trimethyl-4-(phenylsulfinyl)phenyl Ether (6o). 6o** was prepared from the above *tert*-butyldimethylsilyl 2-(3-hydroxypropyl)-3,5,6-tetramethyl-4-(phenylsulfeyl)phenyl ether by oxidation with *m*-CPBA (91%). **6o**: a colorless oil; IR 3400−3200 br, 1547, 1105, 1080, 1042 cm^{-1}; ^1H NMR δ 0.17 (s, 6H), 1.02 (s, 9H), 1.63 (q, J = 6.5 Hz, 2H), 2.09 (s, 3H), 2.32 (s, 3H), 2.41 (s, 3H), 2.73 (t, J = 6.5 Hz, 3H), 3.52 (t, J = 6.5 Hz, 3H), 7.35−7.42 (m, 5H); HRMS calcd for $C_{24}H_{36}O_3SSi$ 432.2154, found 432.2179.

2,6-Diallyl-3,5-dimethyl-4-(phenylsulfinyl)phenyl *tert*-butyldimethylsilyl ether (6q): 49% (three steps) from the corresponding **4**; a colorless oil; IR 1638, 1302, 1084, 1044 cm^{-1}; ^1H NMR δ 0.20 (s, 6H), 1.00 (s, 9H), 2.36 (s, 6H), 3.41 (d, J = 5.0 Hz, 4H), 4.76 (dd, J = 17, 1.5 Hz, 2H), 4.95 (dd, J = 10, 1.5 Hz, 2H), 5.74−5.82 (m, 5H), 7.35−7.43 (m, 5H); HRMS calcd for $C_{26}H_{36}O_2SSi$ 440.2205, found 440.2202.

2,3,5,6-Tetramethyl-1,4-benzoquinone (10a). Typical Procedures for the Preparation of *p*-Quinones 10a,f−j through the Pummerer-Type Reaction. Method A. Under a nitrogen atmosphere, to a solution of **3a** (30 mg, 0.11 mmol) in dry CH_2Cl_2 (3 mL) was added TFAA (0.15 mL, 1.1 mmol) at 0 °C. The reaction mixture was stirred for 10 min. After being diluted with AcOEt (10 mL), the reaction mixture was concentrated. The resulting residue was dissolved in MeOH (3 mL), and saturated aqueous $NaHCO_3$ (four drops) was added. After the mixture was stirred for 1 h, CH_2Cl_2 (10 mL) and saturated aqueous NH_4Cl (four drops) were added, and the mixture was dried with Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography (hexane−AcOEt 10:1) to give **10a** (15 mg, 84%) and diphenyl disulfide (11 mg, 96%).

10a: yellow crystals; mp 110−111 °C (lit.[34] mp 110−111 °C); IR 1636 cm^{-1}; ^1H NMR δ 2.01 (s, 12H).

Method B. Under a nitrogen atmosphere, to a solution of **3a** (27 mg, 0.10 mmol) in CH_2Cl_2 (3 mL) was added TFAA (0.14 mL, 1.0 mmol) at 0 °C, and the reaction mixture was stirred. After 10 min, to the reaction mixture was added MnO_2 (274 mg). The resulting mixture was stirred for 1 h, filtered through a celite pad and concentrated in vacuo. The residue was purified by preparative TLC (hexane−AcOEt 10:1) to give **10a** (10 mg, 62%).

2-(3-Hydroxypropyl)-3,5,6-tetramethyl-1,4-benzoquinone (10f): yellow crystals; mp 41−44 °C (Et_2O−hexane); IR 3200−3000 br, 1644, 1599 cm^{-1}; ^1H NMR δ 1.69 (tt, J = 7.5, 6.0 Hz, 2H), 2.02 (s, 6H), 2.05 (s, 3H), 2.60 (t, J = 7.5 Hz, 2H), 3.58 (t, J = 6.0 Hz, 2H). Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 68.81; H, 7.65.

2-(Ethoxycarbonyl)-3-methyl-1,4-naphthoquinone (10g): dark brown crystals; mp 96−100 °C (Et_2O−hexane); IR 1736, 1669 cm^{-1}; ^1H NMR δ 1.41 (t, J = 7.0 Hz, 3H), 2.19 (s, 3H), 4.45 (q, J = 7.0 Hz, 2H), 7.74−7.78 (m, 2H), 8.07−8.13 (m, 2H). Anal. Calcd for $C_{14}H_{12}O_4$: C, 68.85; H, 4.95. Found: C, 68.59; H, 5.02.

2,3-Bis(ethoxycarbonyl)-1,4-naphthoquinone (10h): yellow crystals; mp 43−46 °C (Et_2O−hexane); IR 1746, 1647, 1593 cm^{-1}; ^1H NMR δ 1.38 (t, J = 7.0 Hz, 6H), 4.42 (q, J = 7.0 Hz, 4H), 7.80−7.85 (m, 2H), 8.10−8.15 (m, 2H); HRMS calcd for $C_{16}H_{14}O_6$ 302.0790, found 302.0790.

2-(*N*,*N*-Diethylcarbamoyl)-3-methyl-1,4-naphthoquinone (10i): yellow crystals; mp 103−105 °C (Et_2O−hexane); IR 1667, 1638, 1632, 1597 cm^{-1}; ^1H NMR δ 1.13 (t, J = 7.0 Hz, 3H), 1.30 (t, J = 7.0 Hz, 3H), 2.16 (s, 3H), 3.18−3.27 (m, 2H), 3.47−3.74 (m, 2H), 7.72−7.79 (m, 2H), 8.05−8.15 (m, 2H). Anal. Calcd for $C_{16}H_{17}NO_3$: C, 70.83; H, 6.32; N, 5.16. Found: C, 70.61; H, 6.35; N, 5.05.

2,3-Bis(*N*,*N*-diethylcarbamoyl)-1,4-naphthoquinone (10j): a yellow gum; IR 1671, 1644, 1593 cm^{-1}; ^1H NMR δ 1.15 (t, J = 7.0 Hz, 6H), 1.20 (t, J = 7.0 Hz, 6H), 3.15−3.49 (m, 6H), 3.62−3.75 (m, 2H), 7.77−7.84 (m, 2H), 8.09−8.15 (m, 2H); HRMS calcd for $C_{20}H_{24}N_2O_4$ 356.1736, found 356.1723.

2-Allyl-3,5,6-trimethyl-1,4-benzoquinone (10e). Typical Procedure for the Preparation of *p*-Quinones 10b−e in the Presence of Allyltrimethylsilane. Under a nitrogen atmosphere, to a solution of **3l** (26 mg, 0.088 mmol) and allyltrimethylsilane (0.14 mL, 0.88 mmol) in dry CH_2Cl_2 (1 mL) was added TFAA (0.12 mL, 0.88 mmol) at 0 °C. The reaction mixture was stirred for 15 min and concentrated in vacuo. Similar to the preparation of **10a**, the residue was treated with saturated aqueous $NaHCO_3$ (method A) and purified to give **10e** (13 mg, 75%) as a yellow oil; IR 1651, 1647 cm^{-1}; ^1H NMR δ 2.02 (s, 6H), 2.03 (s, 3H), 3.26 (d, J = 6.5 Hz, 2H), 4.99−5.12 (m, 2H), 5.77 (ddt, J = 16.5, 10.0, 6.5 Hz, 1H); HRMS calcd for $C_{12}H_{14}O_2$ 190.0994, found: 190.0996.

2,6-Dimethyl-1,4-benzoquinone (10b): pale yellow crystals; mp 71−72 °C (lit.[34] mp 72−73 °C); IR 1653, 1617 cm^{-1}; ^1H NMR δ 2.06 (s, 6H), 6.56 (s, 2H).

2,3,5-Trimethyl-1,4-benzoquinone (10c): pale yellow crystals: mp 28−29 °C (lit.[34] mp 32 °C); IR 1649 cm^{-1}; ^1H NMR δ 1.97−2.01 (m, 9H), 6.53 (brs, 1H).

2-Acetyl-3,5,6-tetramethyl-1,4-benzoquinone (10d): pale yellow crystals; mp 57−59 °C (Et_2O−hexane); IR 1657, 1649 cm^{-1}; ^1H NMR δ 1.98 (s, 3H), 2.03 (s, 3H), 2.05 (s, 3H), 2.42 (s, 3H). Anal. Calcd for $C_{11}H_{12}O_3$: C, 68.74; H, 6.29. Found: C, 68.56; H, 6.26.

Reaction of 3i with TFAA. Under a nitrogen atmosphere, to a solution of **3i** (25 mg, 0.10 mmol) in dry CH_2Cl_2 (1 mL) was added TFAA (0.14 mL, 1.0 mmol) at 0 °C. The reaction mixture was stirred for 15 min, poured into saturated aqueous $NaHCO_3$, and then extracted with CH_2Cl_2. The CH_2Cl_2 layer was washed with brine, dried with Na_2SO_4, and concentrated in vacuo. The residue was purified by flash column chromatography (hexane−AcOEt 10:1) to give **11** (25 mg, 57%) as white crystals: mp 54−56 °C; IR 1800 cm^{-1}; ^1H NMR δ 2.20 (s, 3H), 2.23 (s, 3H), 6.78 (s, 1H), 6.98−7.25 (m, 5H); HRMS calcd for $C_{18}H_{12}F_6O_4S$ 438.0360, found 438.0362.

(34) Minisci, F.; Citterio, A.; Vismara, E.; Fontana, F.; De Bernardinis, S. De *J. Org. Chem.* **1989**, *54*, 728.

Reaction of 3l with TFAA. Under a nitrogen atmosphere, to a solution of **3l** (21 mg, 0.07 mmol) in dry CH_2Cl_2 (3 mL) was added TFAA (0.10 mL, 0.7 mmol) at 0 °C. The reaction mixture was stirred for 10 min and then was concentrated. The residue was purified with flash column chromatography (hexane−AcOEt 10:1) to give **12** (22 mg): IR 3500−3000, 1796 cm^{-1}; ^1H NMR δ 2.05 (s, 3H), 2.11 (s, 6H), 2.94−3.41 (m, 4H), 4.18 (s, 1H), 4.85 (m, 1H), 7.16−7.42 (m, 5H).

Typical Procedure for the ^1H NMR Study on the Pummerer-Type Reaction of 6. Under a nitrogen atmosphere, to an ice-cooled solution of **6c** (23 mg, 0.059 mmol), additive (for runs 11−19, Table 3), and $Cl_2CHCHCl_2$ (15 mg, 0.090 mmol) in $CDCl_3$ (2.0 mL) was added TFAA (0.084 mL, 0.60 mmol). After being stirred for 30 min at 0 °C, the reaction mixture was subjected to ^1H NMR measurement. Yields of **14** and **5** were estimated by comparison of the integration of two couples of their methyl protons and that of the methyne protons of $Cl_2CHCHCl_2$ (δ 5.96).

4-[(*tert*-Butyldimethylsilyl)oxy]-2,3,5,6-tetramethylphenyl Trifluoroacetate (14c) and Its Acetate Derivative. Typical Procedure for the Preparation of *p*-Dihydroquinones 14b−k through the Pummerer-Type Reaction. 14c. Under a nitrogen atmosphere, to a solution of **6c** (23 mg, 0.059 mmol) and styrene (19 mg, 0.18 mmol) in dry $CHCl_3$ (2 mL) was added TFAA (0.084 mL, 0.60 mmol) at 0 °C. The reaction mixture was stirred for 30 min. After being diluted with AcOEt (6 mL), the reaction mixture was concentrated in vacuo to give crude **14c**. Purification by flash column chromatography (hexane → hexane−AcOEt 50:1) gave pure **14c** (18 mg, 79%) as white crystals: mp 84−85 °C (hexane); IR 1800, 1558 cm^{-1}; ^1H NMR δ 0.15 (s, 6H), 1.06 (s, 9H), 2.02 (s, 6H), 2.13 (s, 6H). Anal. Calcd for $C_{18}H_{27}F_3O_3Si$: C, 57.42; H, 7.23. Found: C, 57.61; H, 7.23.

Acetate Derivative of 14c. Crude **14c**, prepared as above, was dissolved in MeOH (8 mL), and saturated aqueous $NaHCO_3$ (4 mL) was added. After being stirred at room temperature for 1 h, CH_2Cl_2 (16 mL) and saturated aqueous NH_4Cl (four drops) were added, and the reaction mixture was dried with Na_2SO_4 and concentrated in vacuo. To the residue were added pyridine (0.24 mL, 3.0 mmol) and Ac_2O (0.24 mL, 2.5 mmol), and the reaction mixture was stirred at room temperature for 5 h and concentrated in vacuo. The residue was purified by column chromatography (hexane−AcOEt 20:1) to give the acetate derivative of **14c** (18 mg, 96%) and 1-phenyl-2-(phenylthio)ethyl acetate **15′** (16 mg, 87%). The acetate derivative of **14c**: white crystals; mp 90−91 °C (hexane); IR 1757 cm^{-1}; ^1H NMR δ 0.13 (s, 6H), 1.05 (s, 9H), 2.01 (s, 6H), 2.11 (s, 6H), 2.33 (s, 3H). Anal. Calcd for $C_{18}H_{30}O_3Si$: C, 67.03; H, 9.38. Found: C, 66.89; H, 9.27.

15′: a colorless oil; IR 1742 cm^{-1}; ^1H NMR δ 2.02 (s, 3H), 3.23 (dd, J = 14.0, 5.5 Hz, 1H), 3.41 (dd, J = 14.0, 8.0 Hz, 1H), 5.88 (dd, J = 8.0, 5.5 Hz, 1H), 7.21−7.40 (m, 10H); HRMS calcd for $C_{16}H_{16}O_2S$ 272.0871, found 272.0879.

4-Methoxy-2,3,5,6-tetramethylphenyl trifluoroacetate (14b): white crystals; mp 82−83 °C (hexane); IR 1798 cm^{-1}; ^1H NMR δ 2.04 (s, 6H), 2.21 (s, 6H), 3.66 (s, 3H). Anal. Calcd for $C_{13}H_{15}F_3O_3$: C, 56.52; H, 5.47. Found: C, 56.39; H, 5.51.

3-Allyl-4-[(*tert*-butyldimethylsilyl)oxy]-2,5,6-trimethylphenyl acetate (14f): yellow crystals; mp 39−40 °C (AcOEt-hexane); IR 1759, 1638, 1250, 1207 cm^{-1}; ^1H NMR δ 0.16 (s, 6H), 1.03 (s, 9H), 2.02 (s, 6H), 2.12 (s, 3H), 2.33 (s, 3H), 3.39 (d, J = 5.5 Hz, 2H), 4.88 (dd, J = 19.0, 2.0 Hz, 1H), 4.95 (dd, J = 12.0, 2.0 Hz, 1H), 5.80 (ddt, J = 19.0, 12.0, 5.5 Hz, 1H). Anal. Calcd for $C_{20}H_{32}O_3Si$: C, 68.92; H, 9.25. Found: C, 69.09; H, 9.13.

4-[(*tert*-Butyldimethylsilyl)oxy]-3-[3-[(*tert*-butyldimethylsilyl)oxy]propyl]-2,5,6-trimethylphenyl acetate (14g): pale yellow oil; IR 1763, 1368, 1210 cm^{-1}; ^1H NMR δ 0.04 (s, 6H), 0.16 (s, 6H), 0.90 (s, 9H), 1.03 (s, 9H), 1.58−1.64 (m, 2H), 2.00 (s, 3H), 2.06 (s, 3H), 2.10 (s, 3H), 2.32 (s, 3H), 2.62−2.66 (m, 2H) 3.62 (t, J = 6.5 Hz, 2H). Anal. Calcd for $C_{26}H_{48}O_4Si_2$: C, 64.95; H, 10.06. Found: C, 65.15; H, 9.88.

3-(3-Acetoxypropyl)-4-[(*tert*-butyldimethylsilyl)oxy]-2,5,6-trimethylphenyl acetate (14h): colorless oil; IR 1769, 1759 cm^{-1}; ^1H NMR δ 0.16 (s, 6H), 1.03 (s, 9H), 1.67−1.79 (m, 2H), 1.99 (s, 3H), 2.04 (s, 6H), 2.10 (s, 3H), 2.32 (s, 3H), 2.68

(t, J = 8.0 Hz, 2H), 4.05 (t, J = 6.5 Hz, 2H). Anal. Calcd for $C_{22}H_{36}O_5Si$: C, 64.67; H, 8.88. Found: C, 64.68; H, 8.78.

4-[(*tert*-Butyldimethylsilyloxy]-2,3,6-trimethyl-5-(3-oxopropyl)phenyl acetate (14i): white crystals; mp 81−83 °C; IR 1761, 1728, 1217 cm^{-1}; ^1H NMR δ 0.17 (s, 6H), 1.00 (s, 9H), 2.00 (s, 3H), 2.04 (s, 3H), 2.10 (s, 3H), 2.33 (s, 3H), 2.56 (t, J = 8.0 Hz, 2H), 2.92 (t, J = 8.0 Hz, 2H), 9.78 (s, 1H); HRMS calcd for $C_{20}H_{32}O_4Si$ 364.2070, found 364.2081.

4-[(*tert*-Butyldimethylsilyl)oxy]-2,6-dimethyl-3,5-dipropylphenyl acetate (14j): colorless oil; IR 1763, 1208 cm^{-1}; ^1H NMR δ 0.18 (s, 6H), 0.90 (t, J = 7.5 Hz, 6H), 1.01 (s, 9H), 1.41 (sext. J = 7.5 Hz, 4H), 2.03 (s, 6H), 2.31 (s, 3H), 2.52−2.62 (m, 4H); HRMS calcd for $C_{22}H_{38}O_3Si$ 378.2590, found 378.2598.

3,5-Diallyl-4-[(*tert*-butyldimethylsilyl)oxy]-2,6-dimethylphenyl acetate (14k): colorless oil; IR 1763, 1638, 1206 cm^{-1}; ^1H NMR δ 0.18 (s, 6H), 1.01 (s, 9H), 2.01 (s, 6H), 2.31 (s, 3H), 3.34−3.45 (m, 4H), 4.83 (dq, J = 17.0, 2.0 Hz, 2H), 4.96 (dq, J = 10.0, 2.0 Hz, 2H), 5.77−5.85 (m, 2H); HRMS calcd for $C_{22}H_{34}O_3Si$ 374.2277, found 374.2279.

Reaction of 6c with Phenylsulfenyl Trifluoroacetate (13). Under a nitrogen atmosphere, to an ice-cooled solution of **6c** (19 mg, 0.049 mmol) in $CDCl_3$ (2 mL) was added a solution of phenylsulfenyl trifluoroacetate generated from CF_3CO_2Ag and PhSCl[30] in $CDCl_3$ (0.18 M, 1.5 mL, 0.28 mmol). After 10 min, the reaction mixture was subjected to ^1H NMR measurement. The yield of **5c** estimated by comparison with $Cl_2CHCHCl_2$ was 70%. **5c:** mp 101−104 °C; IR 1584, 1105 cm^{-1}; ^1H NMR δ 0.17 (s, 6H), 1.07 (s, 9H), 2.17 (s, 6H), 2.40 (s, 6H), 6.88 (d, J = 7.0 Hz, 2H), 7.02 (t, J = 7.0 Hz, 1H), 7.16 (t, J = 7.0 Hz, 2H); HRMS calcd for $C_{22}H_{32}OSSi$ 372.1943, found 372.1936.

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